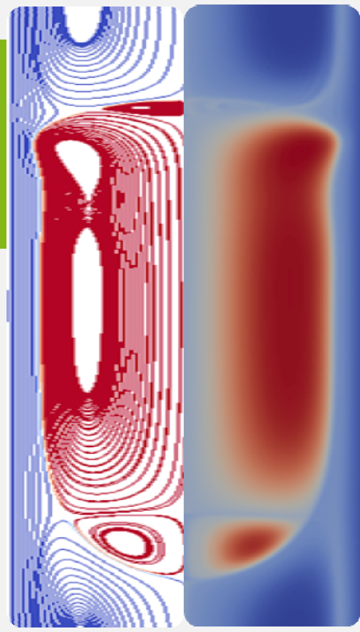
Mass transport in a liquid/liquid slug flow in a micro-capillary reactor



LSA2018, Lübeck

Christian Heckmann,
Peter Ehrhard

Introduction

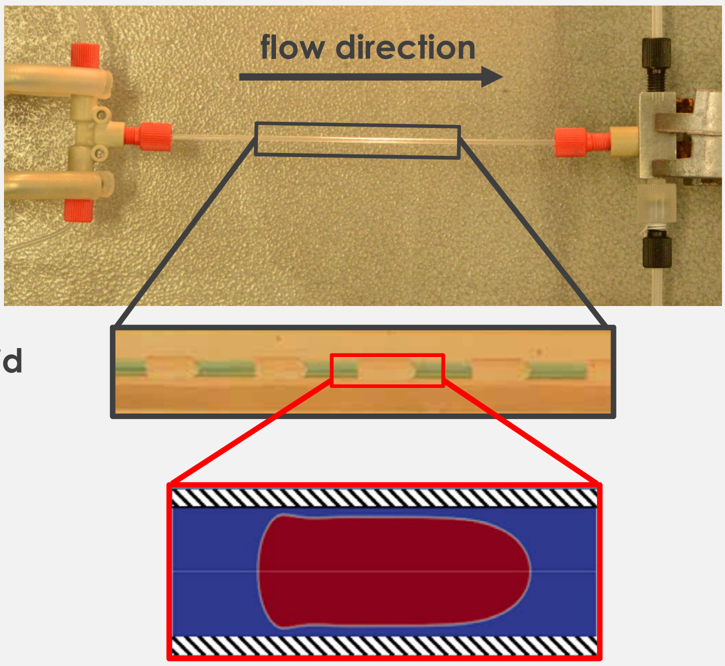
micro-capillary reactor

↓

extraction in liquid/liquid slug flow

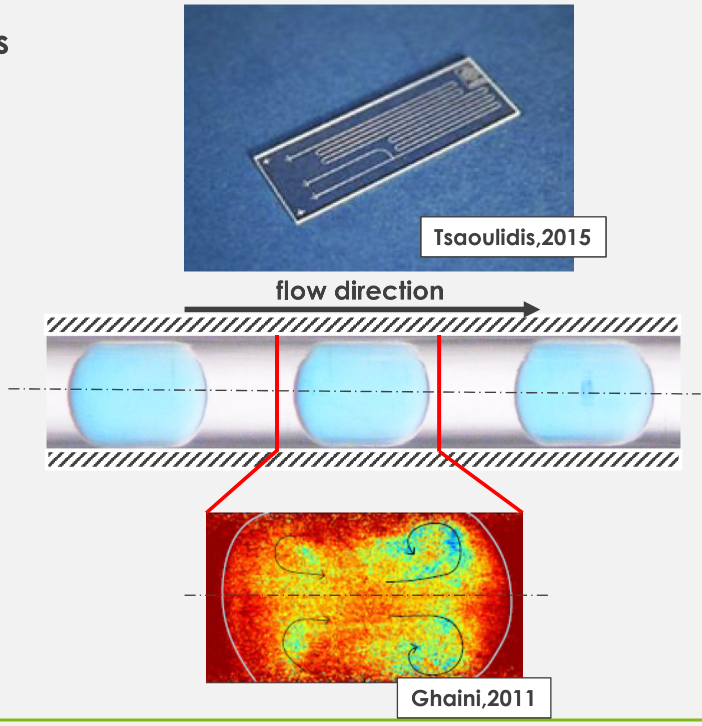
↓

modelling of mass transport



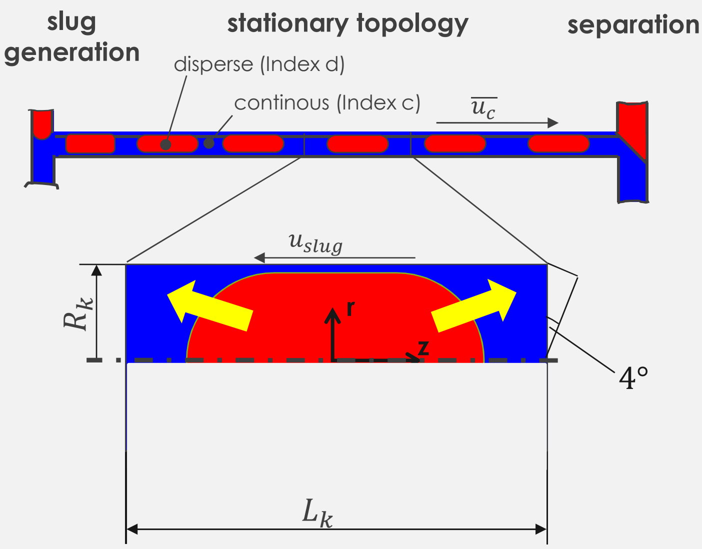
Motivation

- **liquid/liquid extraction systems**
  - limited transport rate
  - long diffusion lengths
- **micro process engineering**
  - short transport lengths
  - large specific surfaces
  - laminar flow
- **slug flow**
  - segmented volumes
  - internal circulation
  - optimal process control



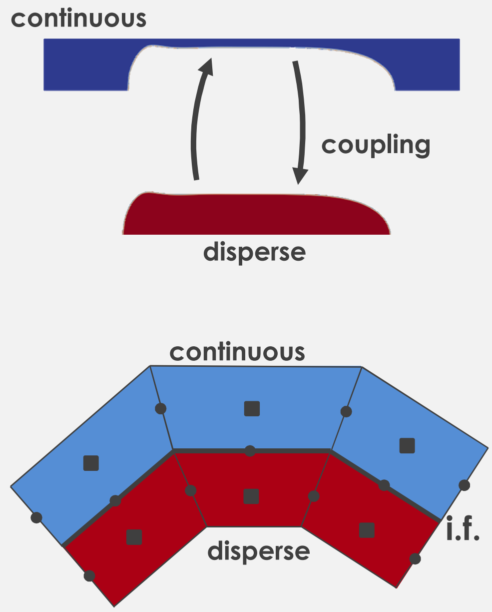
Engineering model

- **periodic element**
  - observer moving with disperse slug
  - rotational-symmetric
  - small diameter
    - little effect of gravity
- **hydrodynamics**
  - two non-miscible incompressible Newtonian liquids
  - laminar flow
  - stationary
  - continuous liquid wets wall
- **mass transport**
  - dilute concentrations ($C \rightarrow 0$)
  - Marangoni effect negligible
  - non-stationary



Simulation – basic idea

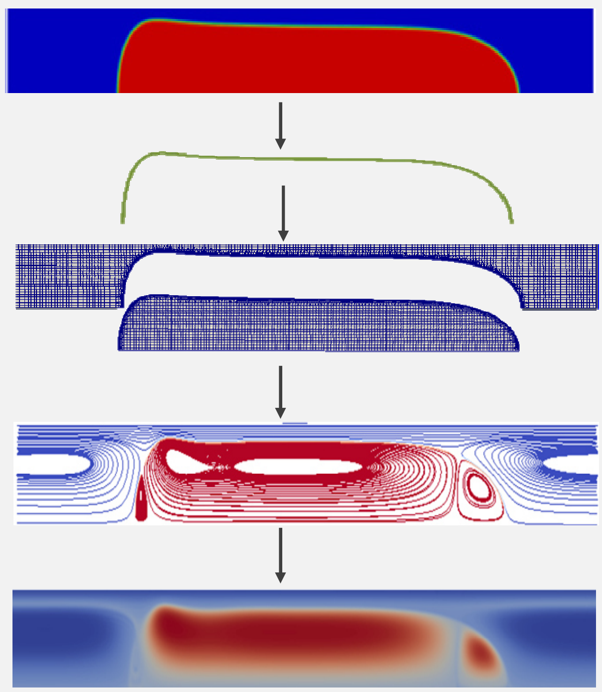
- **interface**
  - idea: surface tracking
  - „sharp“ interface
- **computational domains**
  - one for each phase
  - static domains and meshes
  - coupling at free interface
- **meshes, discretization**
  - finite-volume method (FVM)
  - little numerical diffusion



Simulation - concept

1. **reference simulations** (Dittmar, 2015)
   - stationary hydrodynamics
   - modified level -set method
2. **export interface:**
   - cloud of geometric data points
3. **create adapted meshes**
   - coupled at the free interface
4. **compute hydrodynamics**
   - BC. as in level-set simulations
   - stationary
5. **mass transport**
   - non-stationary
   - one-way coupling

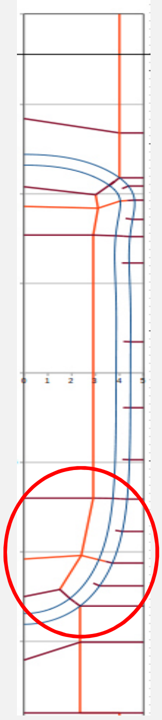
more details follow

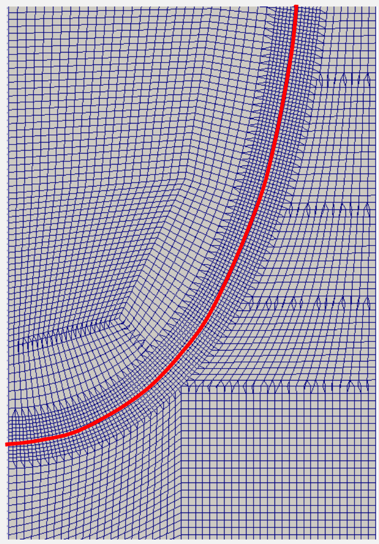


Adapted meshes

- **block-structured comp. domains**
  - fixed structure
  - hexahedrons
  - import cloud of interfacial points
  - corners of blocks adapted

- **adapted meshes**
  - aligned to transport direction
  - coupled at free interface
  - prescribed: resolution around interface
  - additional refinement possible





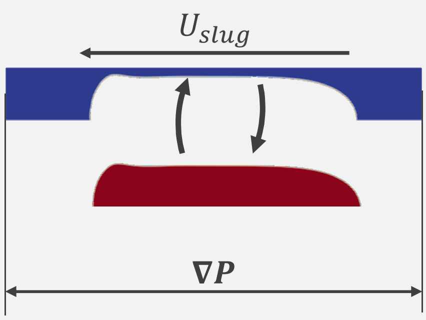
Coupled hydrodynamics

- **conservation equations in each phase**

$$\hat{\rho}\left(\frac{\partial\vec{U}}{\partial\hat{t}}+Re_c\left(\vec{U}\cdot\hat{\nabla}\vec{U}\right)\right)=-\hat{\nabla}P+\hat{\eta}\hat{\Delta}\vec{U} \qquad P=\frac{p\cdot d_k}{\eta_c\cdot u_k}\ ,\ \vec{U}=\frac{\vec{u}}{u_k}\ ,\qquad \hat{\eta}=\frac{\eta}{\eta_c}\ ,\ \hat{\rho}=\frac{\rho}{\rho_c}$$

$$\hat{\nabla}\cdot\vec{U}=0 \qquad Re_c=\frac{u_k\cdot d_k}{\nu_c}\ ,\qquad \hat{\vec{X}}=\frac{\vec{x}}{d_k}\ ,\ \hat{t}=\frac{t\cdot\eta_c}{d_k^2}$$

- **coupling at free interface**
  - contin. phase: $\left.\frac{\partial\vec{U}_{c,GF}}{\partial n}\right|_{GF}=\eta^{`}\left.\frac{\partial\vec{U}_{d,GF}}{\partial n}\right|_{GF},\ \eta^{`}=\frac{\eta_d}{\eta_c}$
  - disperse phase: $\left.\vec{U}_{d,GF}\right|_{GF}=\vec{U}_{c,GF}$



- **iteration of driving pressure gradient** ∇P

Coupled mass transport

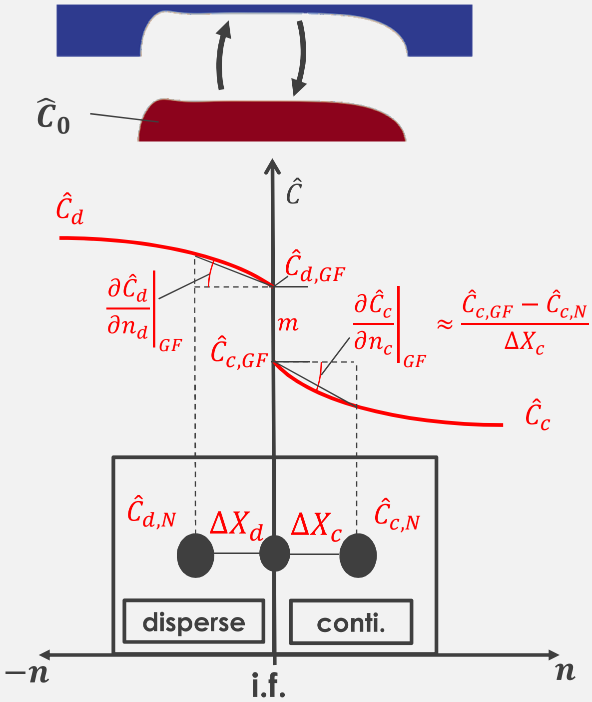
- **initial conditions**
  - disperse phase: $\hat{C}_0 = \frac{C}{C_0} = 1$
- **transport equations in each phase**

$$\frac{\partial \hat{C}}{\partial \hat{t}} + Pe_c\left(\vec{U} \cdot \nabla \hat{C}\right) = \hat{D}\Delta\hat{C}$$

$$Pe_c = \frac{u_k \cdot d_k}{D_c}, \qquad \hat{D} = \frac{D}{D_c}, \; \hat{t} = \frac{t \cdot d_k}{D_k^2}$$

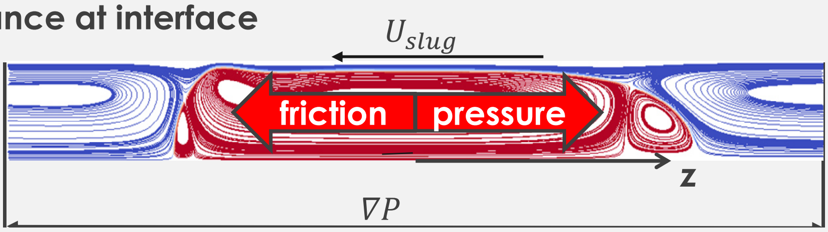
- **coupling at free interface**
  - solubility equilibrium and continuity

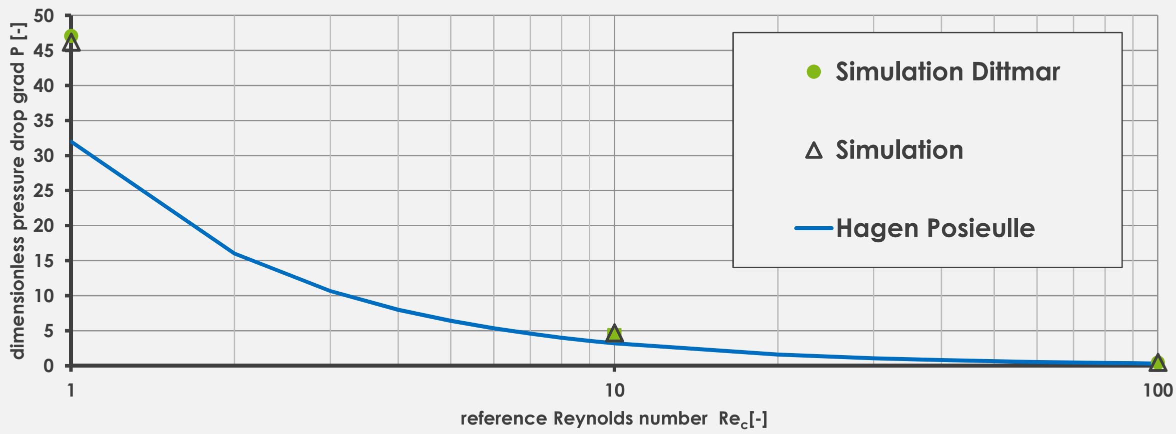
$$\hat{C}_c, GF = \frac{\hat{C}_{d,N}\frac{D'}{\Delta X_d} + \hat{C}_{c,N}\frac{1}{\Delta X_c}}{\frac{D'm}{\Delta X_d} + \frac{1}{\Delta X_c}}, \quad D' = \frac{D_d}{D_c}$$



Validation simulation – hydrodynamics

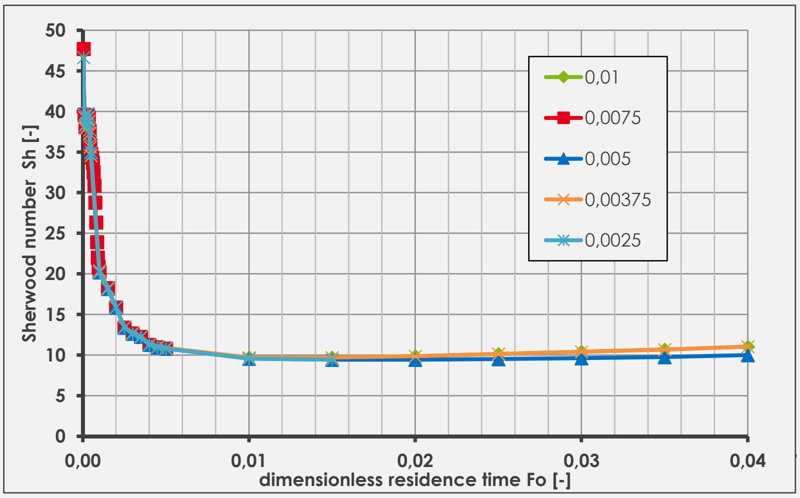
- **force balance at interface**

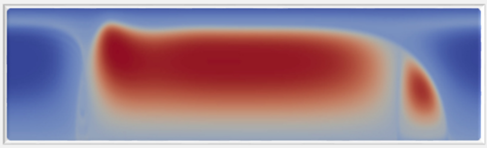


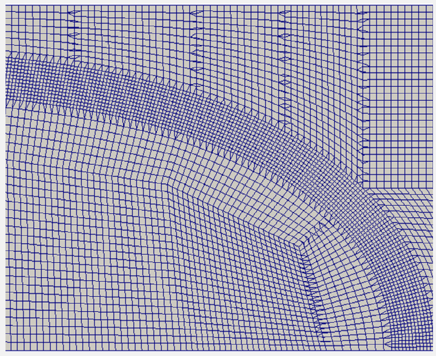


Validation simulation – mass transport

- grid independence study
  - $Pe_c = 10^4; \mathrm{m} = 1, \widehat{D} = 1,$
  - dimensionless resolution $\Delta X = \frac{\Delta x}{d_k}$ + refinement

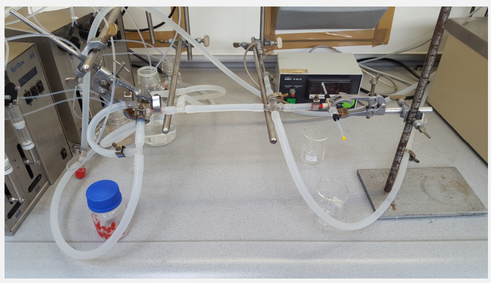


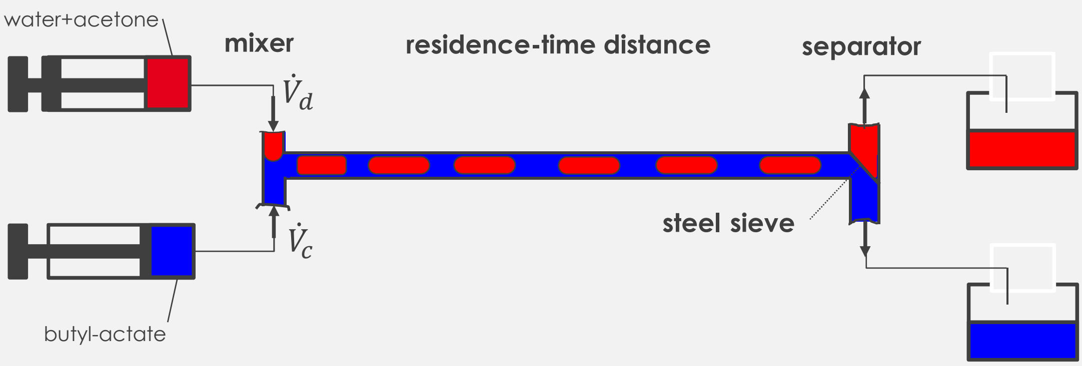




Comparison with experiment

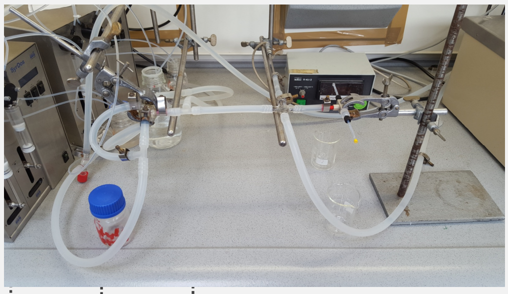
- system: water/acetone/butyl-acetate
- mixer: 180° (PEEK)
- straight capillary: $d_i = 1mm$ (FEP)
- instantaneous phase separation
- extraction: disperse → continuous
- gas chromatography for analysis

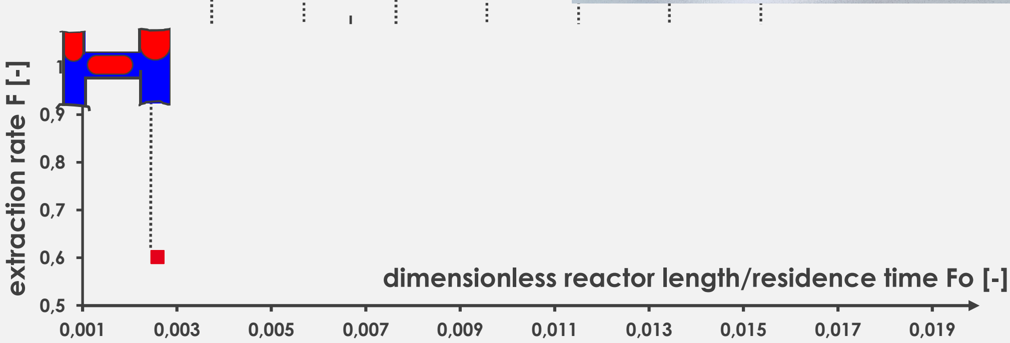




Comparison with experiment

- dilute concentration: $C_0 = 0{,}04\, w.\%$
- phase ration: $R = \frac{\dot{V}_c}{\dot{V}_d} = 1$
- 3 volum. flow rates: $\dot{V}_{ges} = 2; 4; 6\ ml/min$
- extraction evolution
  - reactor length L/residence time





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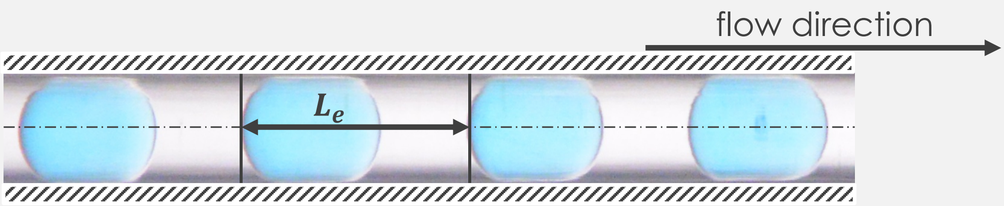
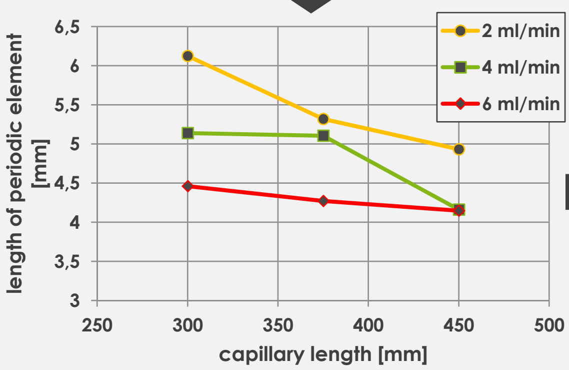
Comparison – element length

- **optical detection:** MATLAB routine





average element length

V [ml/min]	L_e [mm]
2	5,46
4	4,8
6	4,29

Comparison – simulation

- **average species parameters**
  - $\overline{C} = 0{,}02 \frac{kg}{kg}$

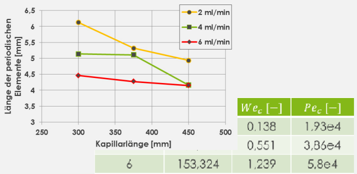
parameters depending on flow rates

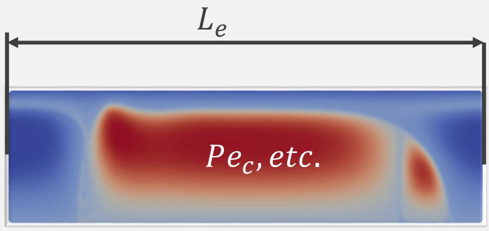
$\dot{V}$ [ml/min]	Re_c [−]	We_c [−]	Pe_c [−]
2	51,108	0,138	1,93e4
4	102,216	0,551	3,86e4
6	153,324	1,239	5,8e4

constant parameters

$\hat{\rho}$	$\hat{\eta}$	$\hat{D}$	m
1,128	1,538	0,454	1

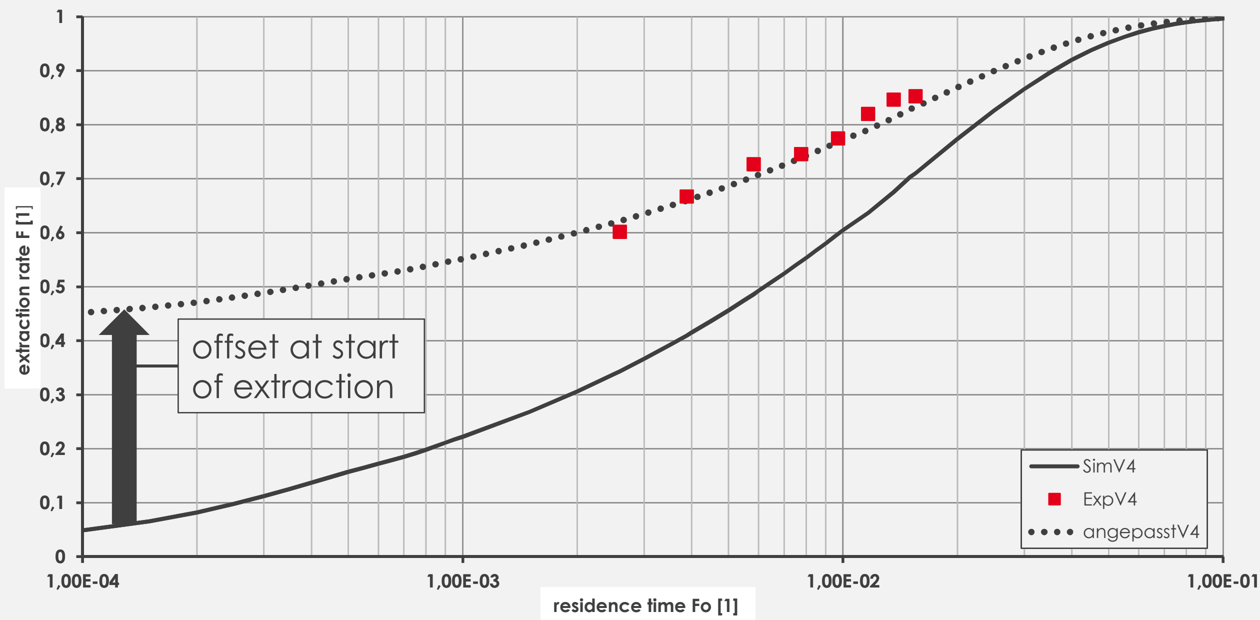
- **specific simulations**



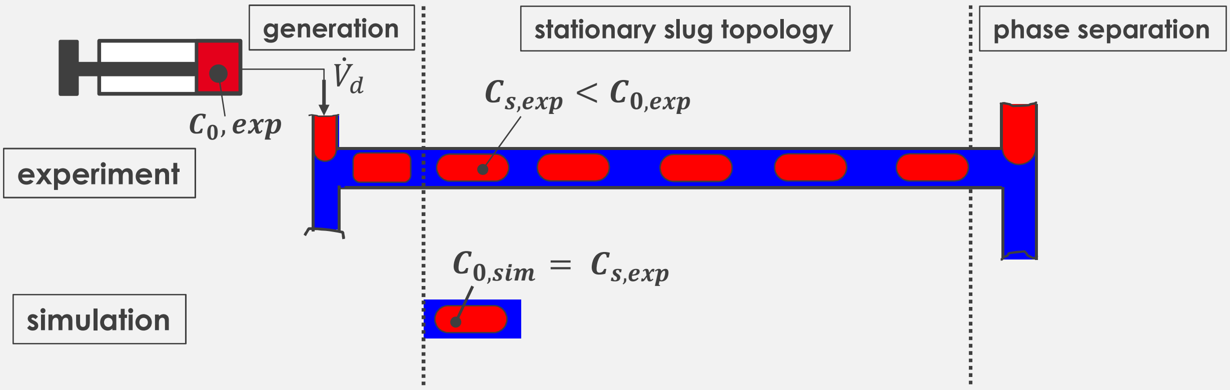


Comparison – effect of generation

- **comparison simulation and experiment: $\dot{V} = 4\ ml/min$**



Comparison – effect of generation



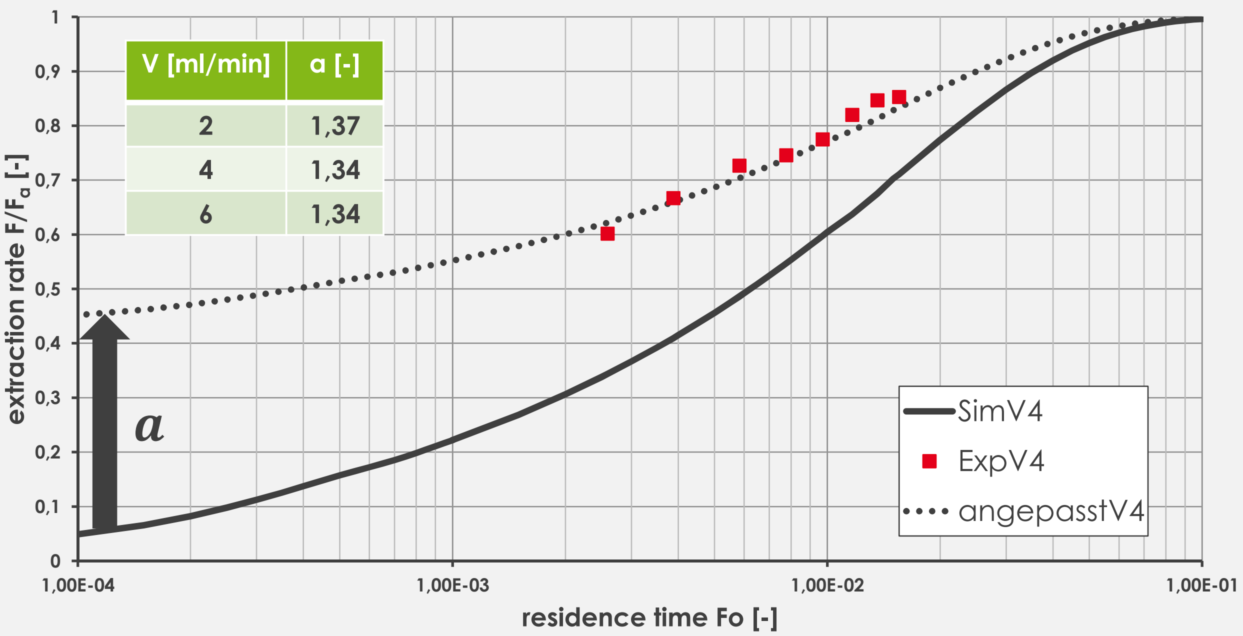
- angle at mixer 180° → intense convection
- system-immanent
- adapted initial concentration for simulations

adaption: $a = \frac{C_{0,exp}}{C_{0,sim}} > 1$ → $F_a = \frac{a \cdot \hat{C}_{0,d} - \bar{\hat{C}}_d}{a \cdot \hat{C}_{0,d} - \hat{C}_{d,\infty}}$

hardly an effect of separation onto extraction

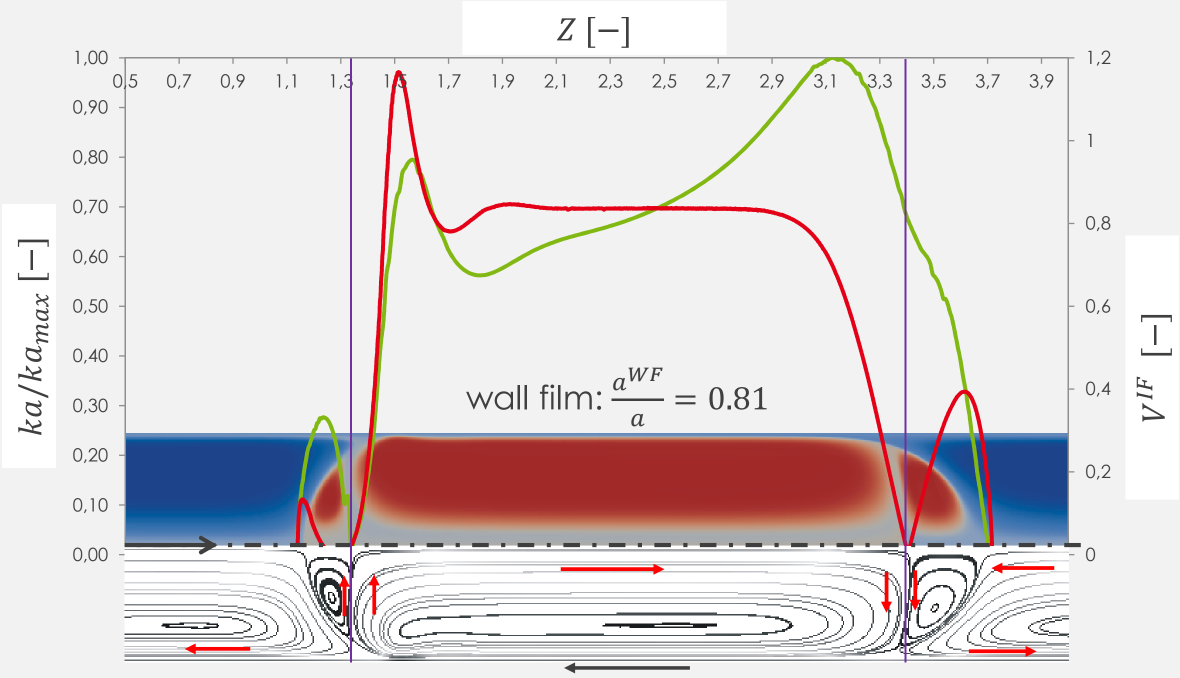
Comparison – effect of generation

- **adaption of initial concentration:** fit by least-square method



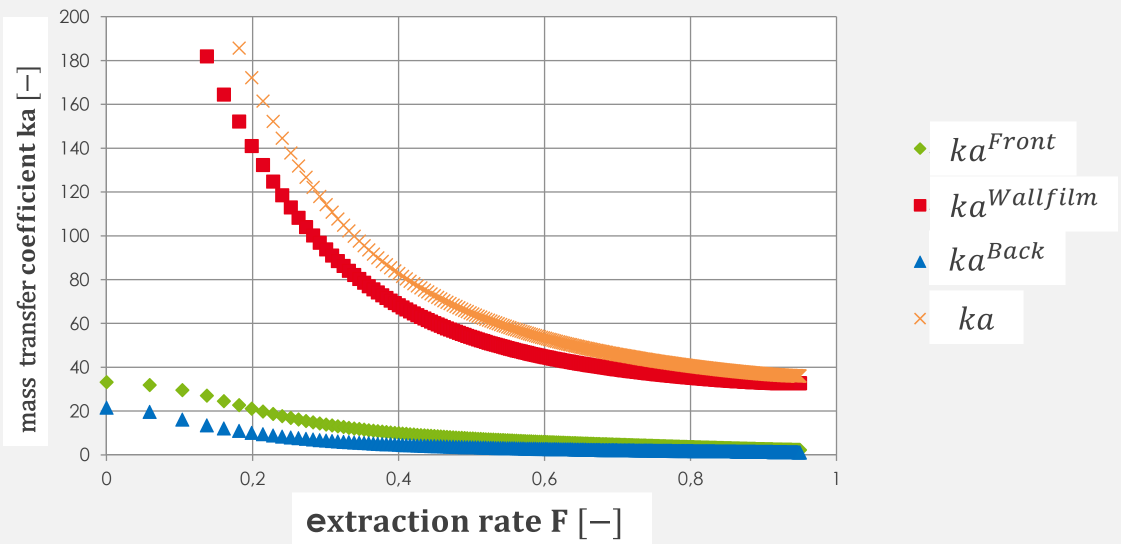
V [ml/min]	a [-]
2	1,37
4	1,34
6	1,34

Local mass transfer



Mass transport in wall film

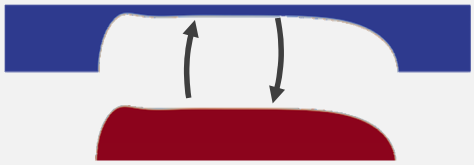
- wall film defined from saddle points of flow field

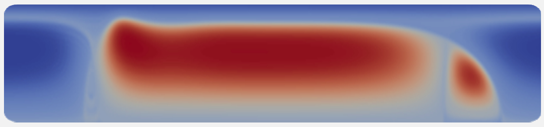


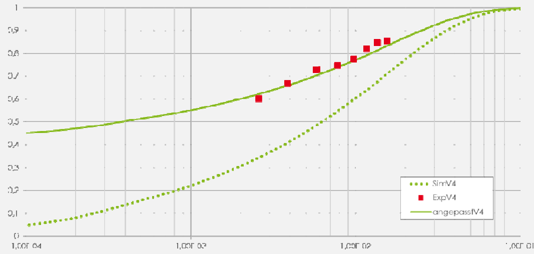
- transport through wall film dominant, end caps have little effect

Conclusion

- **modelling of mass transport**
  - stationary periodic element
  - conjugated mass transfer
  - dilute concentrations
- **numerics**
  - sharp interface
  - separate coupled comp. domains
  - local m.t.: transport dominated by convection
  - local m.t.: transfer to wall film dominates
- **experimental validation**
  - water/acetone/BuAc
  - effect of generation: ~ 33%
  - reactive mass transfer also validated

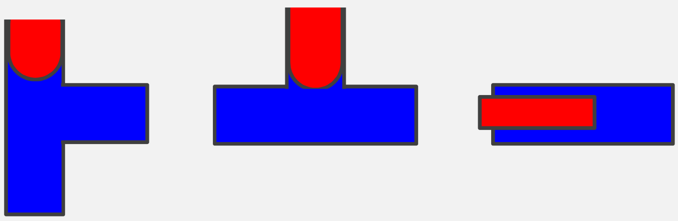






Outlook

- different angle φ in mixer
  - minimize effect of generation
  - already tested with $\varphi = 0$
- reactive mass transfer
  - acid/base titration
  - additional source/sink
  - already validated
- effect of dimensionless groups
  - variation: species/process properties



$\varphi = 180°$ $\varphi = 90°$ $\varphi = 0°$

$$\frac{\partial \hat{C}}{\partial \hat{t}} + U \cdot \nabla \hat{C} = \frac{\hat{D}}{Pe_c} \Delta \hat{C} + r(\hat{C})$$

Thanks for your attention !

Thanks for collaborative validation experiments to:

apparate-
design